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CERTIFICATE

This certificate is issued in support of an application for Patent registration in a country outside New Zealand pursuant to the Patents Act 1953 and the Regulations thereunder.

I hereby certify that annexed is a true copy of the Provisional Specification as filed on 9 September 2002 with an application for Letters Patent number 521269 made by MAGNESIUM TECHNOLOGY LIMITED.

Dated 29 September 2003.

Neville Harris

Neville Harris
Commissioner of Patents, Trade Marks and Designs



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PATENTS ACT 1953

PROVISIONAL SPECIFICATION

THE SURFACE TREATMENT OF MAGNESIUM AND ITS ALLOYS

WE MAGNESIUM TECHNOLOGY LIMITED, a New Zealand company of 137 Captain Springs Road, Onehunga, Auckland, New Zealand, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

TECHNICAL FIELD

The present invention relates to the surface treatment of magnesium and its alloys and uses thereof. The present invention may be particularly suitable for brightening or texturing the surface of articles composed of magnesium or its
5 alloys. However, because the invention may have many uses and/or applications it is to be understood and appreciated that the invention is not to be limited to such use. The prior art and possible applications of the invention as discussed below are therefore given by way of example only.

BACKGROUND ART

10 Magnesium metal, either pure or in an alloy form, is a highly reactive metal. In its usual fabricated forms the surface appearance is relatively dull and obscured by surface oxidation products or other compounds. It does not usually manifest a bright, shiny, metallic finish except when the article has been machined. Although a dull surface may not always be disadvantageous, it is often desirable
15 to provide a bright or polished surface for reasons of aesthetics or utility. Owing to the reactivity of the metal, post-treatments are generally necessary to passivate that surface, and part of the present invention consists of methods whereby this may be done without losing the desired surface finish.

Treatment of magnesium and its alloys has mostly consisted of treatments that
20 result in an anodic coating being applied to the metal, or a paint film, following some kind of pre-treatment process intended to promote paint adhesion. Mostly these processes neither brighten nor polish the metal. Anodising processes for magnesium differ from those employed for aluminium in that the resulting surface is opaque and frequently the coating is inherently coloured. While in
25 many applications this may be a desirable finish in itself, there is no sense in which this could be regarded as polishing or brightening.

Techniques for applying paint to magnesium or its alloys comprise in the main pre-treatments such as chromating or non-chromate conversion treatments, followed by application of a paint. This may be a powder coat, which is electrostatically applied then oven-cured, or a wet paint. The paint may have a shiny finish, but it is not a finish that is comparable to a shiny metallic surface.

Techniques for chemically or electrochemically brightening other metals exist. Methods for brightening aluminium alloy articles are commonly employed in anodising plants. However, these techniques are not applicable to magnesium alloys due to their different chemistry. An approach to brightening aluminium involves a combined acid mixture in which magnesium articles would dissolve rapidly.

It is also possible in some circumstances to chemically or electrochemically plate other metals, for instance, nickel, onto magnesium substrates. Although the resulting plated article has a shiny, metallic appearance, this is due to the plated metal and could not be regarded as a system for brightening or polishing magnesium or magnesium alloy articles. There are also profound disadvantages in plating other metals onto magnesium or magnesium alloy substrates including inter alia galvanic corrosion problems in corrosive environments, expense, processing difficulties in a plating process and high reject rates from most processes.

All references, including any patents or patent applications cited in this specification are hereby incorporated by reference. No admission is made that any reference constitutes prior art. The discussion of the references states what their authors assert, and the applicants reserve the right to challenge the accuracy and pertinency of the cited documents. It will be clearly understood that, although a number of prior art publications are referred to herein, this reference does not constitute an admission that any of these documents form

part of the common general knowledge in the art, in New Zealand or in any other country.

It is acknowledged that the term 'comprise' may, under varying jurisdictions, be attributed with either an exclusive or an inclusive meaning. For the purpose of this specification, and unless otherwise noted, the term 'comprise' shall have an inclusive meaning - i.e. that it will be taken to mean an inclusion of not only the listed components it directly references, but also other non-specified components or elements. This rationale will also be used when the term 'comprised' or 'comprising' is used in relation to one or more steps in a method or process.

10 It is an object of the present invention to address the foregoing problems or at least to provide the public with a useful choice.

Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example only.

DISCLOSURE OF INVENTION

15 According to one aspect of the present invention there is provided a method of polishing and/or brightening magnesium, including the steps of pre-treating the magnesium or magnesium alloy, polishing or brightening the magnesium or magnesium alloy, and passivating the polished or brightened magnesium or magnesium alloy.

20 According to a further aspect of the present invention there is provided a method, substantially as described above wherein said pre-treatment includes a degreasing and/or chemical etching step.

According to a further aspect of the present invention there is provided a method, substantially as described above wherein the polishing or brightening
25 step includes an electropolish.

According to a further aspect of the present invention there is provided a method, substantially as described above wherein said electropolish step involves two steps, the first bring a galvanic polish, and the second involving application of a current.

- 5 According to a further aspect of the present invention there is provided a method, substantially as described above wherein between the pre-treatment and polishing or brightening steps there is provided an optional chemical blast step.

- 10 According to a further aspect of the present invention there is provided a method, substantially as described above wherein said passivation step involves the use of a chemical solution(s).

According to a further aspect of the present invention there is provided a method, substantially as described above wherein the passivation step is an electro passivation step.

- 15 According to a further aspect of the present invention there is provided an article comprising magnesium or a magnesium alloy wherein said magnesium or magnesium alloy is polished or electrochemically brightened by a method substantially as herein described above and in any of the accompanying examples included herein.

- 20 The invention substantially describes a set of methods for chemically and electrochemically brightening or texturing (termed "polishing" herein) the surface of articles composed of magnesium or its alloys. The invention may comprise the steps making up the processes by which the articles are polished and compositions of the chemical solutions that are used, together with details
25 of the imposed electrochemical potential where such a potential is applied.

Table 1: Process Solutions

Name	Code	Composition	Temperature
Phosphoric etch	PE3	Phosphoric acid (H_3PO_4) – 10 mol/l Nitric acid (HNO_3) – 0.5 mol/l	Ambient
Electropolishing solution	EP3	Phosphoric acid (H_3PO_4) – 10 mol/l Monopropylene glycol ($\text{C}_3\text{H}_8(\text{OH})_2$) – 4.5 mol/l	25-35°C
Washing solution	PG1	Monopropylene glycol – 100%	40-60°C
Caustic washing solution	CW25	Sodium hydroxide (NaOH) – 6.25 mol/l	70°C
Passivator 1	PM1	Potassium permanganate (KMnO_4) – 0.25 mol/l Phosphoric acid (H_3PO_4) – to adjust pH to 5-5.5 (added as 5% H_3PO_4)	15-30°C

Passivator 2	PC1	Chromic acid (CrO_3) – 1.8 mol/l Ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) – 0.1 mol/l Potassium fluoride (KF) 0.07-0.15 mol/l	15-30°C
Chemical blast solution	CB1	Ferric chloride (FeCl_3) – 0.12 mol/l Phosphoric acid (H_3PO_4) – 0.8 mol/l	Ambient
Improved chemical blast Solution	CB2A	Ferric chloride (FeCl_3) – 0.16 mol/l Hydrochloric acid (HCl) – 0.05 mol/l Ammonium bifluoride (NH_4HF_2) – 0.06 mol/l Ammonium bromide (NH_4Br) – 0.17 mol/l	Ambient

In the table above, references to concentrations and temperatures are not exclusive. These are the *most preferred values*. The processes operate over a range, both of concentrations and temperatures. Substitutions may be made for chemical constituents; for instance, ethylene glycol may be used in place of
5 monopropylene glycol.

Prior to processing, it is usually appropriate to pre-treat magnesium or magnesium alloy articles to clean and prepare the surfaces for brightening or polishing. The treatment depends on alloy, and the most preferred treatments are summarised below for some common alloys and forming processing.
10 Alternative treatments may be possible and in some cases, depending on

original surface condition of the article; the omission of one or more steps may be without adverse effect on subsequent processing steps.

TABLE 2: RECOMMENDED PRE-TREATMENTS

Forming Process	Alloy	Pre-treatment Steps		
		Description	Compound	Conditions
Die casting (<i>for bright or metallic finish</i>)	91	Degrease	CW25	1-2 min
		Rinse	H ₂ O	
		Phosphoric Etch	PE3	30-60 seconds
		Rinse	H ₂ O	
Die casting (<i>for bright or metallic finish</i>)	AM50/60	Degrease	CW25	1-2 minutes
		Rinse	H ₂ O	
		Phosphoric Etch	PE3	30 seconds
		Rinse	H ₂ O	
Rolled sheet (<i>for bright or metallic finish</i>)	AZ31	Degrease	CW25	1-2 minutes
		Rinse	H ₂ O	
		Phosphoric Etch	PE3	Up to 2 minutes
		Rinse	H ₂ O	

Extrusion (<i>for bright metallic finish</i>)	AZ31	Degrease Rinse	CW25 H ₂ O	1-2 minutes
All alloys (<i>chemically blasted finish</i>)		As for bright metallic finish plus: Rinse Rinse	 CW25 H ₂ O	 30-45 seconds

Following pre-treatment, the article may be polished to a bright or metallic finish, or chemically blasted by a selective etch to give a light, textured finish similar to shot blasting.

The method of producing these finishes is fundamentally similar in each case
5 and may be summarised in the following table.

TABLE 3: SUMMARY OF PROCESS SEQUENCE FOR ELECTROPOLISHING,**METALLIC FINISH AND CHEMICAL BLAST FINISH**

Forming Process	Alloy	Finish	Process steps		
			Description	Compound	Conditions
1. Chemical blasting (after this step, articles are electropolished in #2)					
(a) Die casting Extrusion Rolled sheet	AZ91 AM50 AM60 AZ31	Chemical 1 blast	Activation	CB2A	1 minute
			Chemical blasting	CB1	2-10 minutes
			Chemical blasting 2	CB2A	1 minute
			Caustic wash	CW25	1-2 minutes
			Rinse	H2O	
(b) Extrusion Rolled sheet	AZ31	Chemical 1 blast	#1 (a) steps then:		
			Phosphoric etch	PE3	1.5-2.5 minutes
			Rinse	H2O	
2. Electropolish					
Die casting	AZ91	Bright finish	Galvanic polish	EP3	8 minutes
			AC current	EP3	15-20 seconds

		Chemica l blast	#1 (a) steps then: AC current Galvanic polish AC current	EP3 EP3 EP3	2 minutes 3-4 minutes 15-20 seconds
		AM50 Bright finish	Galvanic polish AC current	EP3 EP3	6 minutes 15-20 seconds
		AM60			
		Chemica l blast	#1 (a) steps then: AC current Galvanic polish AC current	EP3 EP3 EP3	1 minute 2-3 minutes 15-20 seconds
	Rolled sheet	AZ31 Bright finish	Galvanic polish	EP3	30 seconds
			AC current	EP3	10 seconds
			Galvanic polish	EP3	20 seconds
			AC current	EP3	10 seconds
Extrusion	AZ31	Bright finish	Galvanic polish	EP3	50-60 seconds
			AC current	EP3	10 seconds
		Chemica l blast	#1 (a), 1 (b) steps then as for bright finish	EP3	50-60 seconds

				EP3	10 seconds
Die casting	AZ91	Metallic finish	Galvanic polish	EP3	4-5 minutes Note: No AC current
		C-blast metallic	#1 (a) steps then: Galvanic polish	EP3	3-5 minutes
	AM50	Metallic	Galvanic polish	EP3	3.5-4 minutes
	AM60	CB metal	#1(a) then gal pol	EP3	2-3 minutes

3. Monopropylene glycol rinse (subsequent to steps 1, 2 or step 2 as appropriate)

Die casting	AZ91	Bright	Rinse		
Extrusion	AZ31	Metallic		PG1	3-5 secs (one brief dip)
Die casting	AM50	Bright	Rinse		
	AM60	Metallic		PG1	5-7 secs (with stirring)

4. Caustic wash (subsequent to above steps 1-3 or 2-3 as appropriate)

All	All	All	Caustic wash	CW25	20-30 seconds
			Rinse	H2O	

5. Passivation (subsequent to above steps 1-4 or 2-4 as appropriate)

Die casting	AZ91	Bright	Passivate	PC1	7-10 secs
		Metallic	Passivate	PC1	30-60 secs

	AM50	Bright	Passivate	PM1	7-10 secs
	AM60	Metallic	Passivate	PC1	30-60 secs
All	All	All	Electropassivate	NH ₄ HF ₂	30 secs, 10-20 volts
Extrusion	AZ31	All	Passivate	PC1	30-60 secs
6 Final steps (subsequent to 1-5 or 2-5 as appropriate)					
All	All	All	Rinse	H ₂ O	
			Dry	Hot air	

The "electropolish" step in the table involves two separate treatments that may be conducted in one process vessel. The first of these is a "galvanic polish" in which the article is short-circuited to a copper counter-electrode immersed in the EP3 solution. During the galvanic polish there is no externally imposed current.

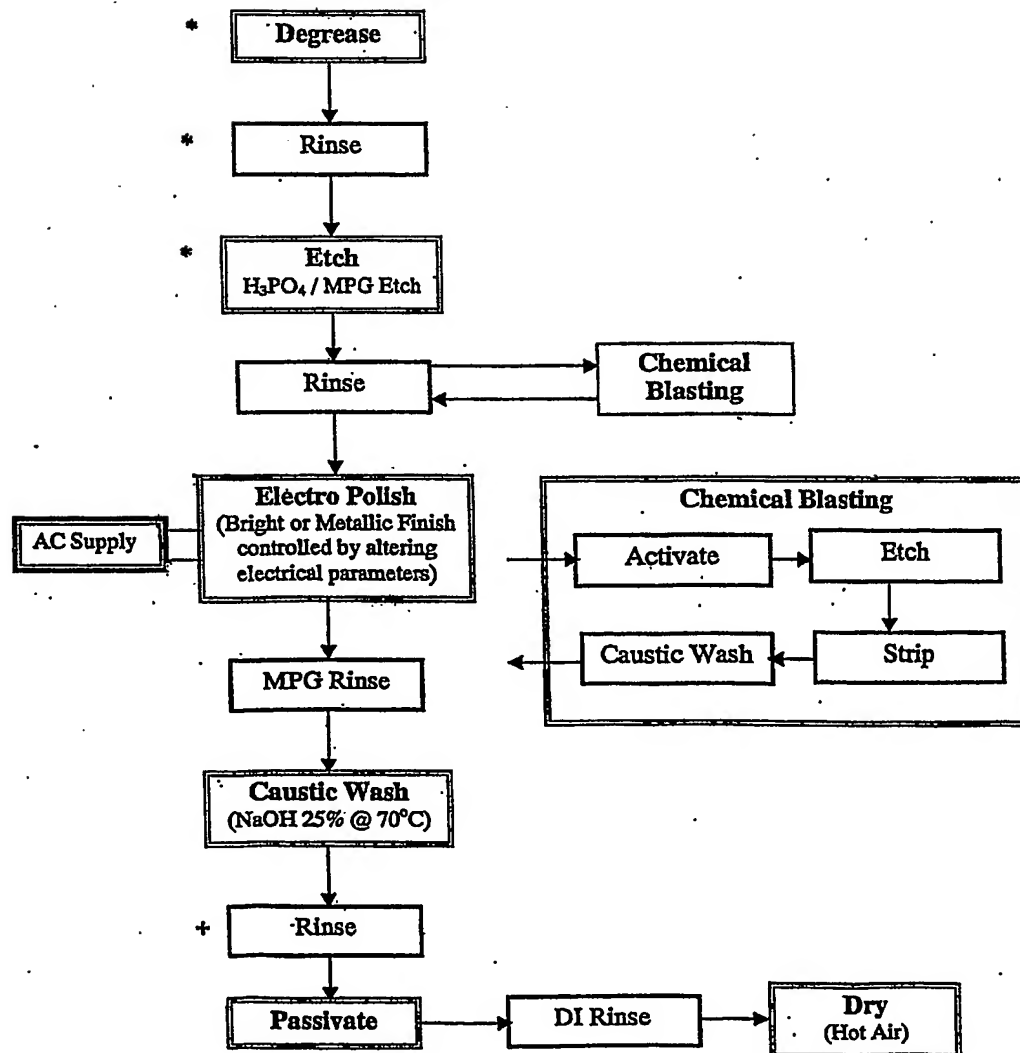
- 5 The second treatment conducted during the electropolishing comprises the imposition of an AC voltage, at 5 Vac. The current is not controlled and reaches a value that depends on the surface area of the work being processed and the characteristics of the surface and alloy. A current density of 750 to 1,500 A/m² may be expected. A copper counter-electrode may be used in the electrochemical
- 10 cell.

Passivation of the brightened, metallic or chemically blasted surface may be undertaken chemically, using either of the two chemical solutions listed above or by means of an electropassivation step. In this a DC voltage of approximately 10-20 volts may be applied to the article, which is made the anode of a circuit in

15 a solution of 2% ammonium bifluoride (NH₄HF₂·2H₂O) at ambient temperature, for 30 seconds (refer to diagram 1 below). A stainless steel counter-electrode

having at least twice the surface area of the article being passivated is employed. The electropassivation method avoids the use of heavy metals and provides substantially good corrosion resistance.

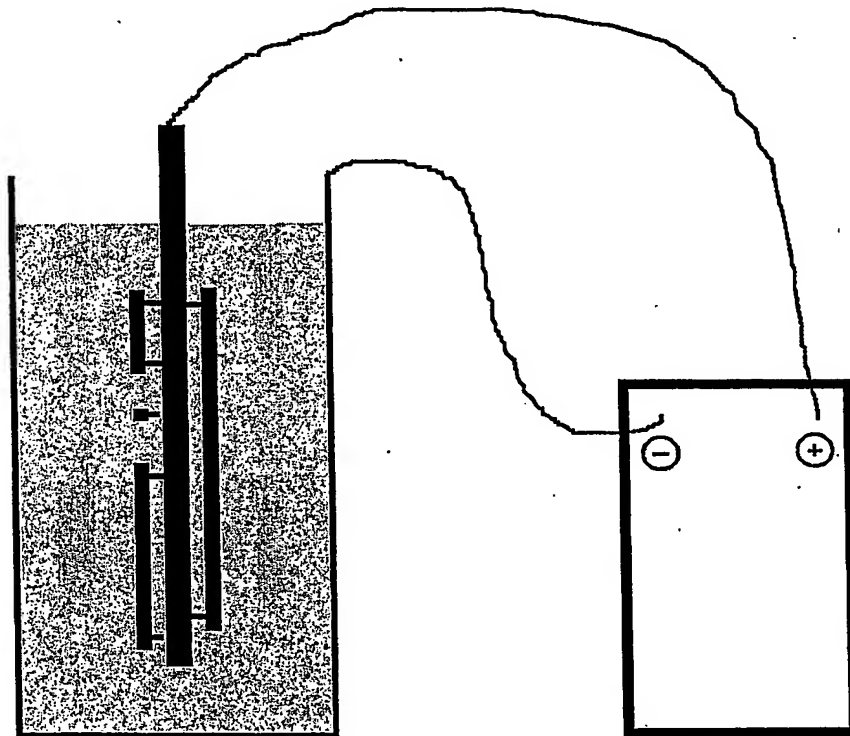
FIGURE 1: PROCESS FLOWCHART



The flowchart may be read in conjunction with the foregoing tables for details of times, temperatures and process solutions applicable to each step. The examples (antes) provide more detail.

DIAGRAM 1: ELECTROPASSIVATION

5



Articles to be passivated are connected to a conductive busbar which is made the anode of an electrochemical cell. The articles must be fully immersed in the solution, which is 2% ammonium bifluoride (NH_4HF_2) in water. A DC potential
10 of 10-20 volts is applied to the articles for 30 seconds.

TEST MODES

The following set out various examples and steps involved in treating magnesium and it's alloys to achieve a brightened surface finish. They are not definitive, and have been used as examples only to illustrate potential methodologies.

1. A die cast plate, 140mm x 100mm, 3mm thick, of AM50 alloy, was brightened, using the following steps:
 - Degrease in CW25 at 70°C for one minute
 - Rinse in water for approximately 30 seconds
 - 10 • Pre-etch in PE3 for 30 seconds
 - Rinse in water
 - Electropolish in EP3 solution in two stages – galvanic polish (no imposed AC voltage) for six minutes, followed by an imposed AC voltage of 5 VAC for 20 seconds.
 - 15 • Rinse in monopropylene glycol for 5 seconds
 - Wash in CW25 for 20 seconds at 70°C
 - Rinse in water
 - Passivate, using potassium permanganate solution, PM1, for 10 seconds
 - Rinse in water
 - 20 • Dry using hot air

The result was a very bright finish, having a slight yellow tinge. The die cast structure was plainly visible.

5 2. A die cast plate of AZ91D alloy having the same dimensions as in example 1 supra, was treated using the following processes:

- Degrease in CW25, 70°C, for 1 minute
- Rinse in water
- Pre-etch in PE3 for 30 seconds
- Rinse in water
- 10 • Polish in EP3 solution for 5 minutes, using a galvanic polish (no AC voltage)
- Rinse in monopropylene glycol for 5 seconds
- Wash in CW25, 70°C for 20 seconds
- Rinse in water
- 15 • Passivate using PC1 for 30 seconds
- Rinse in water
- Dry using hot air

The result was a metallic finish in which casting structures were visible.

3. A die cast plate of AM50 alloy, having the same dimensions as that in examples 1 and 2 supra, was treated using the following processes:
- Degrease in CW25 at 70°C for 1 minute
 - Rinse in water
- 5
- Pre-etch in PE3 for 30 seconds
 - Wash in CW25, 70°C for 30 seconds
 - Rinse in water
 - Chemical blast in three steps – 1 minute in CB2A solution followed by 7 minutes in CB1 solution and finally, an additional minute in CB2A solution
- 10
- Wash in CW25, 70°C, 1 minute
 - Polish in EP3 solution in three steps – one minute using an imposed AC voltage of 5 VAC, 3 minutes without AC voltage, then an additional 20 seconds using an imposed AC voltage as before.
- 15
- Rinse in monopropylene glycol for 5 seconds
 - Wash in CW25, 70°C for 20 seconds
 - Rinse in water
 - Passivate in PM1 for ten seconds
 - Rinse in water
- 20
- Dry using hot air

The result was a bright finish, with a high degree of texturing which obscured most of the die cast structures. Examination through a microscope revealed a surface topography of sharp ridges adjacent to rounded pits.

5

4. A rolled flat plate, of AZ31B alloy, 110mm x 80mm, 1mm thick was pre-conditioned so that it was clean of sundry corrosion and dirt. It was then processed as follows:

- Degrease in CW25, 70°C for one minute
- 10 • Rinse in water
- Pre-etch in PE3 for 15 seconds
- Rinse in water
- Polish using four steps – 30 seconds without AC, followed by 10 seconds using an imposed AC voltage of 5 VAC, another 20 seconds without AC
- 15 and finally, a further 10 seconds with the AC voltage as before
- Rinse in monopropylene glycol for 5 seconds
- Wash in CW25, 70°C for 30 seconds
- Rinse in water
- Passivate in PC1 for 30 seconds
- 20 • Rinse in water
- Dry using hot air

The result was a mirror bright finish.

5. A flat plate, AM50 alloy, of the same dimensions as those in example 1 supra, was processed using the following treatments:

- 5 • Degrease in CW25, 70°C for one minute
- Rinse in water
- Pre-etch in PE3 for 15 seconds
- Rinse in water
- 10 • Polish in EP3 solution in two stages – galvanic polish (no imposed AC voltage) for six minutes, followed by an imposed AC voltage of 5 VAC for 20 seconds.
- Rinse in monopropylene glycol for 5 seconds
- Wash in CW25 for 20 seconds at 70°C
- Rinse in water

15 The plate was then passivated by an electrochemical treatment. It was immersed in a solution of 2% ammonium bifluoride ($\text{NH}_4\text{HF}_2 \cdot 2\text{H}_2\text{O}$) which was contained in a plastic tank with attached stainless steel plates on each side. These were connected to the negative terminal of a suitable power supply while the article itself was attached to a bus bar that was connected to the
20 positive terminal. After twenty seconds, the power was switched on and maintained at 15 VDC (± 1 VDC). Upon the application of the electric current the article became noticeably brighter. There was no gas evolution. Initially the current was 20 A, but this decayed to around 1 A after 5 seconds and

finally to about 0.3 A after 30 seconds. At this time the power was switched off,
the plate was removed from the solution, rinsed with deionised water and
dried. The article was bright and shiny in appearance with no obvious surface
film. However, its passivity was obvious when tested using reagents towards
5 which magnesium metal articles are normally highly reactive.

MAGNESIUM TECHNOLOGY
LIMITED

by their Attorneys

JAMES & WELLS

Jeremy Sin

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